

EFFECT OF THE AMOUNT OF BASE SITE ON CATALYTIC BEHAVIOR OF CaO FOR SYNTHESIS OF DIMETHYL CARBONATE FROM PROPYLENE CARBONATE AND METHANOL

Tong Wei Wei Wei* Mouhua Wang Yuhan Sun
Bing Zhong

State Key Laboratory of Coal Conversion Institute of Coal Chemistry Chinese Academic of Sciences, Taiyuan, 030001

Introduction

Dimethyl carbonate (DMC) is a unique molecule having versatile chemical property and has been used mainly as methylating and methoxycarbonylating agent substituting for toxic phosgene, dimethyl sulfate, or methyl iodide [1-3]. It can be synthesized by transesterification method, in which CO₂ reacts with propylene oxide to yield propylene carbonate (PC), which continually reacts with methanol (MeOH) to yield DMC[4,5]. The reaction of PC with MeOH can be catalyzed by solid base with high conversion and selectivity [6]. On the basis of the discussion in the other paper submitted to this meeting, the effect of the amount of base site on catalytic behavior of CaO for synthesis of DMC from PC and MeOH was investigated in detail.

Experimental

CaO was prepared from CaCO₃ calcined at 1073K or 1173K in N₂ atmosphere. The reaction was carried out in a 250mL flask equipped with reflux condenser, water bath and magnetic stirring. Catalyst was added into the flask accompanied with violent magnetic stirring after the temperature reached to the expected one. Reaction product was analyzed by Gas Chromatograph after centrifugal separation of solid catalyst from liquid.

Results and discussion

It was reported that CaO calcined from CaCO₃ was super base. Thus in present paper, CaO was prepared from CaCO₃ calcined at 1073K and 1173K respectively. BET surface area of CaO was listed in Tab. 1; XRD and CO₂TPD results of CaO were illustrated in Fig.1, 2. It can be seen from Fig.1 that CaCO₃ was totally dissociated when calcined at 1073K for 1hr and yields cubic CaO. Both the extendedness of calcinations time and the increase of temperature result in surface area increase as shown in Tab.1. From Fig.2 we can see that there is four kinds of base site with CO₂ desorption temperature being 430K, 470K, 640K and 890K respectively. With the extendedness of time and the increase of temperature, the amount of base site increases greatly with the sequence being 1173K/2hr > 1073K/2hr > 1073K/1hr.

Tab.1 BET Surface area of CaO obtained from CaCO₃ calcined under different condition(m²/g)

Calcination temperature/K	Calcination time /hr	BET Surface Area /m ² . g ⁻¹
1073	1	3.848
1073	2	12.706
1173	1	12.166

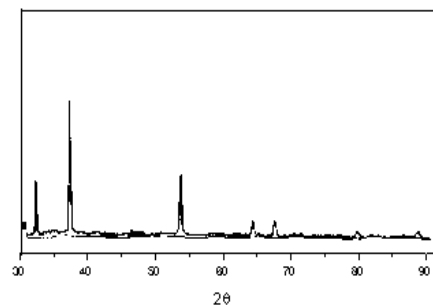


Fig.1 XRD of CaO calcined from CaCO₃ at 1073K for 1hr

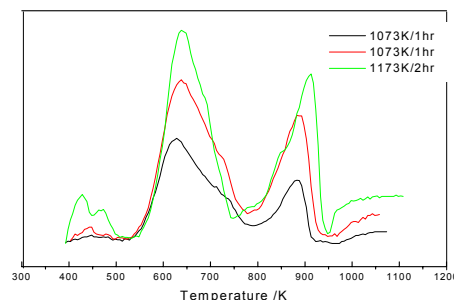


Fig. 2 CO₂ TPD of CaO calcined from CaCO₃

Since this reaction usually catalyzed by strong base, the effective base site may be that with CO₂ desorption temperature being 640K and 890K respectively. The effect of the amount of base site on DMC yield, DMC selectivity and reaction rate was shown in Fig. 3-5. It can be seen that with the increase of the amount of base site, the time need to reach equilibrium was shortened while equilibrium DMC yield was unchanged, which means the increase of the amount of base site can result in the increase of reaction rate but not change the equilibrium. On the other hand, the DMC selectivity decreases gradually with the increase of the amount of base site. The base site can catalyze both the subject reaction and the polymerization of PC, therefore the increase of base site will also promote the side reaction and consequently make the DMC selectivity decrease. Fig. 5 shows the effect of the amount of base site on the reaction rate, with the increase of the amount of base site, the maximum rate increase and the induction time was shortened. As side in the other paper, the induction time comes from the activation of MeOH, the increase of base site amount can not only promote the activation of MeOH, but also make the surface concentration of activated MeOH increase and consequently promote the surface reaction of PC with activated MeOH.

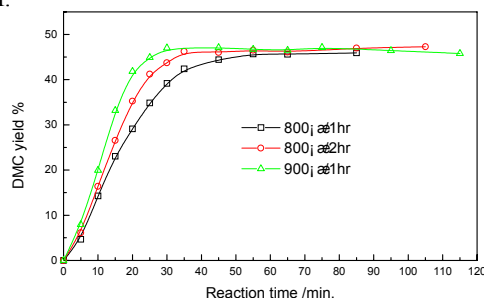


Fig. 3 Effect of basicity on DMC yield

* To whom corresponding should be addressed. Fax: +86 351 4041153

E-Mail: yhsun@sxicc.ac.cn or weiwei@sxicc.ac.cn

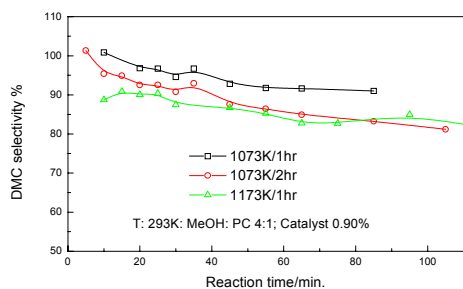


Fig.4 Effect of basicity on DMC selectivity

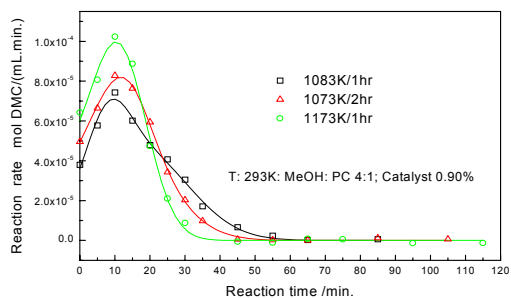


Fig. 5 Effect of basicity on reaction rate

Conclusion

1. CaCO_3 calcined at 1073K and 1173K can yield cubic CaO, which shows excellent catalytic activity for synthesis of DMC from PC and MeOH.
2. Both the surface area and the amount of base site of CaO increase with the increase of calcination temperature and the extendedness of calcination time for CaCO_3 .
3. The increase of the amount of base site can promote both subject reaction and side reaction, therefore although the reaction rate increases, the DMC selectivity decreases with the increase of the amount of base site.

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